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**(54) Title:** RINSE AGENTS THAT FORM CLEAR COATINGS ON WARE

**(57) Abstract**

The composition and method of use of a rinse agent including an aqueous solution of an effective deposit modifying amount of a deposit modifier that causes the formation of a clear coating of deposits are described. Clear coatings are prepared in form on the surface of the ware after ware is contacted with the rinse agent of the invention in a rinsing stage.

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## RINSE AGENTS THAT FORM CLEAR COATINGS ON WARE

### FIELD OF THE INVENTION

5        This invention relates to rinse agents for warewashing. More specifically, the invention relates to deposit modifiers that cause the formation of a clear coating of non-volatile deposits on the surface of the ware after a rinsing stage.

10

### BACKGROUND OF THE INVENTION

Mechanical washing equipment is used in typical household, institutional, and industrial warewashing or dishwashing. Commonly available dishwashing machines  
15 have mechanical spray mechanisms by which ware is sprayed with a cleaning solution in a cleaning stage followed by a rinsing solution in a rinsing stage. Generally, in dishwashing machines, both the cleaning solution and rinsing solution are held in machine  
20 reservoirs, pumped to a spray mechanism where the cleaning and rinsing solution are directed under pressure in turn onto the ware. See U.S. Patent No. 4,811,738 (Copeland). After rinsing, the rinse solution can be recycled and used in the cleaning stage. These  
25 dishwashing machines can employ a variety of scraping, cleaning, rinsing and other steps. However, most machines operate with two or more steps of the following sequence: scraping, rinsing, washing, rinsing and sanitizing.

30        Rinse agents (or rinse aid, rinse additives, or sheeting agents) are normally low foaming substances commonly added to the rinse water to produce a rinsing or "sheeting action" which ensures substantial rinse water removal and to aid in the minimization or  
35 prevention of filming, streaking or spotting caused by residual detergent, food soil, and mineral solids in the rinse water. The precise mechanism by which rinse agents cause the rinse water to form continuous sheets which drain cleanly from the surface is not clearly

established. Conventional rinse aids typically comprise a low foaming surface active agent made from homopolymers or copolymers of an alkylene oxide such as ethylene oxide or propylene oxide or mixtures thereof.

5 See U.S. Patent No. 4,711,738 (Copeland).

These conventional rinsing agents reduce spotting and filming of ware and decrease the necessary time to dry the dishes. This sheeting action is provided by about 50 to 200 ppm of a nonionic surfactant, which must  
10 be an efficient wetting agent and low foaming. Additionally, sequestering agents have been used in similar concentrations to inhibit the formation of visible deposits on the ware during the drying process. These conventional rinse agents perform by preventing  
15 any type of visible deposit formation on the surface of the ware. U.S. Patent No. 4,711,738 (Copeland), describes the use of rinse compositions for warewashing containing an active halogen compound and low foaming rinse agent comprising an alkyl diphenyl oxide sulfonic  
20 compound. U.S. Patent No. 3,629,127 (Palmer et al.) describes the preparation of low foaming rinse additives from a blend of certain nonionic and anionic surfactants. U.S. Patent No. 4,750,942 (van Dijk et al.) describes the use of a non-plate-shaped colloid in  
25 a rinse aid composition. U.S. Patent No. 4,492,646 (Welsh) describes the preparation of anionic and nonionic surfactant compositions. Rinse Aids, Parker and Schoene, Happi (January 1988) pages 83-86, disclose the use of rinse aids to prevent spotting and filming of  
30 glassware. Parker et al. teach there is no solution to the problem of streaking and filming of glassware with high solids water. Non-Phosphate ADDs by Shulman, Happi (July 1992) pages 130-138 describes homo- or copolymers of acrylic and maleic acids as complexing agents in  
35 automatic dishwasher detergents. Shulman describes the use of complexing agents to clean the surface before

rinsing, and no attempts were made to solve the high solids water problem.

Problems are associated with these conventional rinse agents, however, when the service water contains medium to high levels of mineral solids including calcium and magnesium. At total dissolved solids levels greater than 600 ppm, the many rinse aids of the prior art will not prevent streaking and spotting. See Rinse Aids, Parker and Schoene, Happi (January 1988), pp. 83-86.

Conventional rinse agents function by causing rinse water to sheet and drain from the ware. The presence of an aqueous rinse agent prevents the formation of a visible film of deposits during the rinsing process. However, in high solids water, these conventional rinse agents can be totally ineffective in preventing the forming of deposit films. See Parker and Schoene, cited above. Thus, there is a substantial need in the warewashing industry for a rinse aid that prevents the appearance of filming, streaking, and spotting of ware during the rinsing stage in high solids water.

#### SUMMARY OF THE INVENTION

The invention is directed to a rinse agent having a deposit modifier that minimizes, reduces or prevents the appearance or formation of undesired, visually perceptible film, streaks or spots on ware and its use thereof. The improved method of warewashing involves contacting ware with a cleaning solution in a cleaning stage, and then contacting the ware with an aqueous rinse agent in a rinsing stage.

The improved rinse agent includes an aqueous solution of a deposit modifier that causes the formation of a clear coating of deposits.

The rinse agent of the invention includes an effective deposit modifying amount of the deposit modifier to cause the formation of a clear coating of

mineral deposits to form on the surface of the ware article. Within the context of the invention, the term clear refers to something that is substantially invisible to the naked human eye and visible only with the help of optics.

The rinse agent generally includes an aqueous solution of 300 to 20,000 ppm of a deposit modifier having sequestering properties. Preferably, the concentration of the deposit modifier in the rinse agent is about 1,000 to 8,000 ppm. More preferably, the concentration of the deposit modifier in the improved rinse agent is about 2,000 to 6,000 ppm, and most preferably, the concentration of the deposit modifier is about 3,000-4,000 ppm.

Preferably the ppm ratio of the deposit modifier to the total dissolved mineral in the aqueous solution is between 2:1 to 6:1. The deposit modifier of the invention can also be of a food grade.

The deposit modifier causes a clear coating of non-volatile deposits to remain on the ware after the rinsing stage. More preferably, the clear coating of deposits has an average thickness of about 5 nm to 2  $\mu$ m.

The rinse agent is effective in high solids service water, containing dissolved solids levels of less than about 1,500 ppm. In contrast to the prior art rinse agents, the rinse agents of the invention are effective above 600 ppm total dissolved solids.

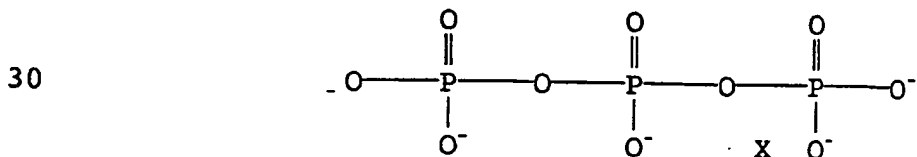
The rinse agent can further include a corrosion protecting agent, a soil release promotion agent, a coating stabilization agent and mixtures thereof.

The invention is also directed to a method of warewashing utilizing the rinse agent of the invention, a clear coating of deposits formed from the deposit modifier and an article of ware resulting from the warewashing method of the invention.

DETAILED DESCRIPTION OF THE INVENTIONTHE DEPOSIT MODIFIER

An improved rinse agent according to the invention comprises an aqueous solution of an effective deposit modifying amount of a deposit modifier. Within the context of the invention, an effective deposit modifying amount of the deposit modifier is preferably a sufficient amount to cause a clear coating of deposits to form on the ware after the rinsing stage. Generally, the rinse agent comprises about 300 to 20,000 ppm of a deposit modifier comprising a compound having hydrogen-bonding properties. Preferably the deposit modifier comprises at least three hydrogen bonding groups selected from the group consisting of a carboxy, a phospho, a phosphono, amino, hydroxy, sulfo, sulfono, derivatives thereof and mixtures thereof. The three or more hydrogen bonding groups can be: -COOH, -COOH and -COOH; -COOH, -COOH and -OH; or -COOH, -SO<sub>3</sub> and -NH<sub>2</sub>, for example. The deposit modifier can be selected from two general formulas I and II described hereafter.

In Group I, the deposit modifier comprises two carboxy groups and at least one additional hydrogen bonding group selected from the group consisting of a carboxy, a phospho, a phosphono, a hydroxy, an amino, a sulfo, a sulfono, derivatives thereof and mixtures thereof. In Group II, the deposit modifier comprises a compound of the general formula



wherein X is at least 1, preferably 1 to 20.

In a preferred embodiment, the deposit modifier is selected from the group consisting of the sodium salts of: tripolyphosphate, ethylene diamine tetraacetic acid, nitrilo triacetic acid, citric acid, lactic acid, gluconic acid, 2-phosphonobutane-1,2,4-tricarboxylic

acid, 1-hydroxyethylidene-1,1-diphosphonoic acid, hexametaphosphate, tartaric acid, aspartic-N,N-diacetic acid, beta-alanine-N,N-diacetic acid, malic acid, sulfosuccinic acid, and aspartic acid, polymers or  
5 copolymers of acrylic acid, maleic acid and acrylamide methyl propane sulfonate; and the sugars: sorbitol, galactose, maltose, glucose, sucrose and lactose.

The improved rinse agent of the invention can also have about 300 to 20,000 ppm of a mixture of two or more  
10 deposit modifiers comprising compounds having sequestering properties wherein the deposit modifiers comprise one or more functional groups selected from the group consisting of a carboxylate, a phosphate, a phosphonate, amino, hydroxy, sulfo, sulfono, and  
15 derivatives thereof. Preferably the deposit modifiers in the mixture of two or more deposit modifiers are selected from the group consisting of the sodium salts of: tripolyphosphate, ethylene diamine tetraacetic acid, nitrilo triacetic acid, citric acid, lactic acid,  
20 gluconic acid, 2-phosphonobutane-1,2,4-tricarboxylic acid, 1-hydroxyethylidene-1,1-diphosphonoic acid, hexametaphosphate, tartaric acid, aspartic-N,N-diacetic acid, beta-alanine-N,N-diacetic acid, malic acid, sulfosuccinic acid, and aspartic acid, polymers or  
25 copolymers of acrylic acid, maleic acid and acrylamide methyl propane sulfonate; and the sugars: sorbitol, galactose, maltose, glucose, sucrose and lactose. More preferably, the mixture of two or more deposit modifiers comprises sodium gluconate and sodium citrate.

30

#### THE IMPROVED RINSE AGENT

The rinse agent of the invention comprises an effective deposit modifying amount of a deposit modifier comprising a compound having sequestering properties.  
35 In a preferred embodiment the rinse agent comprises an aqueous solution of 300 to 20,000 ppm of the deposit modifier comprising a compound having sequestering



properties. Significantly, the rinse agent of the invention can be surfactant free. A surfactant is unnecessary to practice the invention, and preferably, there is less than one part by weight of a low foaming surfactant, having sheeting properties, in the rinse agent for every ten parts of all other components in the rinse agent excluding water. More preferably, there is less than one part of such surfactant per 20 parts of all other components excluding water, and most preferably less than 1 part surfactant per 100 parts of all other components excluding water.

Preferably the concentration of the deposit modifier in the aqueous solution is about 1,000 to 8,000 ppm. More preferably, the concentration of the deposit modifier is about 2,000 to 6,000 ppm, and most preferably the concentration of the deposit modifier in the aqueous solution is about 3,000 to 4,000 ppm.

The water that makes up the aqueous portion of the improved rinse agent can have a wide range of total dissolved solids including mineral solids in the water. The rinse agents of the invention are effective when the total dissolved solids level in the water are less than about 2,500 ppm, preferably less than about 1,500 ppm.

In a typical embodiment of the present invention, the ppm ratio of the deposit modifier to the total dissolved solids in the water is from about 2:1 to 6:1. Specifically, the preferred ratio of the deposit modifier to the total dissolved solids depends on several factors including which deposit modifier is being used in the rinse agent and in some cases the pH level at which the rinse agent is being utilized.

#### CONCENTRATED LIQUID AND SOLID FORMS

The deposit modifiers of the invention can be made up as a concentrated aqueous liquid or solid source. These concentrated sources of the deposit modifier can

be diluted with or dissolved in water to form the improved rinse agent of the invention.

Typically, the concentrated liquid forms of the deposit modifiers have about 10 to 60% actives dissolved in the water. Specifically, in a preferred concentrated aqueous source of sodium citrate, there is about 50 to 60% actives in the concentrated liquid. Alternatively, a concentrated liquid source of a 1:1 mixture by weight of sodium tripolyphosphate and hexametaphosphate comprises about 50% actives in the liquid concentrate. In an additional embodiment, a concentrated liquid source of the mixture of sodium gluconate and gluconic acid comprises about 50 to 60% actives in the liquid concentrate. In a further embodiment, a concentrated liquid source of sodium tripolyphosphate can have about 10 to 13% actives in the liquid source. The upper limits on actives in the concentrate are dictated by solubility considerations because it is undesirable to have the actives precipitating from the liquid concentrates.

A solid source of the deposit modifiers of the invention can also be utilized. The solid sources of the deposit modifiers can have up to about 90% actives. Preferably, the solid source has about 60 to 80% actives with the other 20 to 40% being a casting agent. The casting agents can be selected from, but not limited to, the group consisting of homopolymers or copolymers of an alkylene oxide.

### DEPOSIT DISTRIBUTION

The rinse agent of the invention causes a clear coating of mineral deposits to remain on the ware after the rinsing stage. Preferably the clear coating of deposits has an average thickness of about 5.0 nm to 2.0  $\mu\text{m}$ . More preferably, the clear coating of deposits has no substantial differences in the refractive index throughout the coating. The ware with the clear coating

was examined by illumination with light and the clear coating appeared to be amorphous.

The clear coating of the invention comprises:

- (a) non-volatile components from a service water;
- 5 (b) a deposit modifier; and
- (c) water.

Table I, shown below, summarizes various embodiments of the invention, which are aqueous solutions (850 ppm total dissolved mineral solids in the  
10 water) of various deposit modifiers.

Typically, the ware materials that were washed, rinsed and examined (to determine the nature of the film reported in Table I) were a china dinner plate, a melamine dinner plate, a glass panel, a stainless steel  
15 panel, a stainless steel butter knife and a 10 oz. glass tumbler. However, most of the time, only a glass panel is used because spots and films on glass are detected by dark-field illumination in which light impinges on the glass panel at a shallow angle from underneath and  
20 observation is made at a high angle with respect to the direction of light.

First, the water tank capacity of the warewashing machine was determined. Then the wash rack and the ware materials were placed inside the washing machine.  
25 Typically, the service water used for the preparation should be at about 160 to 180 °F.

The warewashing machine was filled to capacity with the service water. A 2% LIME-A-WAY solution (containing phosphoric acid) was then added to the warewashing  
30 machine. Thus, for every 10 liters of service water, this involved adding 200 grams of LIME-A-WAY. The ware materials were then washed for 3 minutes, and the washing machine drained and refilled with clean service water.

35 The ware materials were then washed for 3 minutes with the clean service water, and then the washing machine was drained and refilled. Next 0.2% by weight

of a GUARDIAN PLUS detergent (comprising tripolyphosphate and caustic soda), manufactured by Ecolab, was added to the warewashing machine. For every 10 liters of service water, this required 20 grams of the GUARDIAN PLUS detergent. The ware materials were washed for 3 minutes, and then the warewashing machine was drained and refilled with clean service water. The ware materials were then washed with the clean service water for 3 minutes, and the warewashing machine was drained and refilled with clean service water. This step was repeated two more times. The preparation of the ware materials for testing was completed, and the test rack was removed from the warewashing machine.

The concentration of a deposit modifier to be added to the service water was then determined. The warewashing machine was filled to capacity with clean service water, and the test rack containing the ware materials was placed in the warewashing machine.

The proper amount of the deposit modifier was then added to the wash water to achieve the desired concentration of actives in the wash water. The warewashing machine was turned on and the water sprayed for about 60 seconds. The warewashing machine was then stopped, and the water drainage from the ware materials was observed.

In the evaluation of the ware materials, a scale from 1 to 4 was used. A clarity of 1 indicates that the ware material had no visible coating to the naked eye. A clarity of 2 indicates to the evaluator that there was a partial visible film on the surface of the ware, and a clarity of 3 indicates a thick film of mineral deposits on the surface of the ware. A value of 4 indicates that there were a few intense specks of crystalline mineral deposits on the surface of the ware.

These clarify evaluations were conducted shortly after the drying of the ware was completed. After significant periods of time at high temperature or

humidity, crystalline material can form in the clear film. The actual amount of time before the crystals develop varies with each deposit modifier, but the time decreases as the temperature and humidity increase.

5        In the examples in Tables I, II and III, the softened well water containing about 350 ppm TDS (total dissolved solids) was supplemented by additional solids made of equal weights of sodium chloride and sodium sulfate. The level of TDS is as indicated in each table.

10       For a high solids service water with a TDS of 850 ppm, Table I shows that different compounds yield different forms of deposits on glass. They can be a clear coating, mild to heavy films, or dense specks surrounded by clear regions. In general, multidentate  
15       sequesters perform best (e.g. EDTA, sodium tripolyphosphate), while simple salts (sodium chloride, sodium carbonate) leave heavy films after drying.

         However, Table II shows a wide range of tolerance to TDS in service water for a variety of deposit  
20       modifiers at 3,000 ppm. Table III shows that the efficiency of various deposit modifiers are different, depending on their molecular structure and molecular weight. For example, to overcome a service water with  
25       800 ppm TDS, only 2,000 ppm of sodium citrate would be needed, while over 4,000 ppm of sodium gluconate would be required to get a clear coating.

TABLE I  
Clarity of Coating from Various Deposit Modifiers

5	3,000 ppm of Deposit Modifier Used in Aq. Sol.	Clarity*	
		pH# of Coating	
	Sodium tripolyphosphate	9	1
	Hexametaphosphate	6	1
10	EDTA	6	1
	Nitrilo triacetic acid	10	1
	Sodium Citrate	8	1
	Gluconic Acid	8	1
	2-phosphono butane-1,2,4-tricarboxylic acid	3	1
15	1-hydroxyethylidene-1,1-diphosphonic acid	1	1
	Aspartic-N,N-diacetic acid	12	1
	Beta-alanine-N,N-diacetic acid	7	1
	Tartaric acid	2	1
	Sorbitol	8	1
20	Sulfosuccinic acid	7	1
	Aspartic acid	7	1
	Malic acid	2	1
	Acumer 2000 (Rohm & Haas, a copolymer of acrylic acid and AMPS)	5	2
25	Polyacrylate	6	2
	Glycolic acid	8	2
	Lactic acid	10	2
	Sodium Pyrophosphate	9	2
	Sodium phosphate	10	2
30	Potassium tripolyphosphate	8	2
	Potassium pyrophosphate	9	2
	Malic acid	11	2
	Acusol 505 N (Rohm & Haas, a copolymer of acrylic and maleic acids)	8	2
35	Polyacrylate	7	2
	Gluconic acid	6	2
	Glucose	8	2
	Lactose	8	2
	Sucrose	8	2
40	Malic acid	9	2
	Galactose	8	2
	Glycolic acid	8	2
	Succinic acid	7	2
	Urea	8	3
45	Sodium hydroxide	13	3
	Sodium carbonate	12	3
	Sodium metasilicate	12	3
	Sodium chloride	8	3
	Glycerol	8	3
50	Glycine	5	3
	Oxalic acid	1	3
	Maleic acid	7	3

TABLE I (CONT'D)  
Clarity of Coating from Various Deposit Modifiers

5	3,000 ppm of Deposit Modifier Used in Aq. Sol.	Clarity* pH# of Coating	
10	Sodium xylene sulfonate	7	N
	Sodium cumene sulfonate	7	N
	Propylene glycol	8	N
	Glycolic acid	2.5	N
	Lactic acid	4	N
15	Propionic acid	1	N
	Maleic acid	1	N
	Succinic acid	3	N
	Monoethanolamine	11	N
	Diethanolamine	10	N
20	Triethanolamine	9	N
25	# The aqueous solution of deposit modifiers is brought to the indicated pH with NaOH.		
	* Clarity Scale Used:		
	1-clear		
30	2-light film		
	3-dense uneven film		
	N-few intense specks due to non-sheeting drainage		
35	Total dissolved solids in water is 850 ppm.		

TABLE II  
Tolerance of Deposit Modifiers Towards TDS

5	3,000 ppm of Deposit Modifier Used in Aq. Sol.	ppm of TDS to show film (clarity of > 1)
10	Galactose, pH 8	300
	Acusol 505N, pH 8 (copolymer of acrylic and maleic acids)	500
	Polyacrylate pH 7	600
15	Gluconic acid, pH 6	600
	Glucose, pH 8	700
	Lactose, pH 8	700
	Malic acid, pH 11	700
	Acumer 2000, pH 7	700
20	(copolymer of acrylic and AMPS)	
	Sucrose, pH 8	600
	Sodium sulfosuccinate, pH 7	1,000
	Sodium aspartate, pH 7	1,500
25		

TABLE III  
Efficiency of Deposit Modifiers

30	TDS, ppm in water	ppm of deposit modifier needed to get a clear coating		
35	gluconate	Na citrate	STPP	Na
	600	1,200	2,200	2,400
	800	1,800	2,800	3,300
40	1,000	2,400	3,600	4,300
	1,300	3,400	4,800	6,300

45 ADDITIONAL COMPONENTS

The improved rinse agent of the invention can further comprise additional components selected from the group consisting of a surfactant, a corrosion protecting agent, a soil release promotion agent, a coating

50 stabilization agent, and mixtures thereof. These additional components are not critical or required for practice of the invention, but can be incorporated into



practice of the invention, but can be incorporated into the rinse agent as necessary to achieve benefits other than improved rinsing.

The rinse agents of this invention can also contain, if desired, diluents and additives. For example, perfumes, enzymes, dyes, antitarnishing agents, antimicrobial agents, and the like, may be added without detracting from the advantageous deposit modifying properties of the invention.

10

#### METHOD OF WAREWASHING

The invention is also directed to a method of warewashing utilizing the rinse agent of the invention. Warewashing machines which can be used in the method are well known, and can use many different types and forms of detergents including: liquid, powder and block. Such warewashing machines include, but are not limited to, a Hobart C-44 manufactured by Hobart Corporation of Troy, Ohio. In household and commercial warewashing operations, washing of ware comprises at a minimum two stages, a washing stage and a rinsing stage.

A washing stage is usually performed using aqueous solutions or suspensions of highly alkaline detergent compositions and water maintained at an elevated temperature. The washing stage can be commonly performed at a relatively low temperature, i.e., at 120° to 160°F, or at a relatively high temperature, commonly 160° to 200°F.

In the rinsing stage, the ware is contacted with the rinse agent for a sufficient period of time to displace the residual wash solution remaining on the ware. The ware should be contacted with the rinse agent for a sufficient amount of time to displace the residual wash water from the ware. Preferably, the ware is contacted for at least about 10 to 15 seconds, more preferably at least about 30 seconds.

The temperature of the improved rinse agent is typically about 120°F to 200°F. Preferably, the temperature is about 140°F to 180°F. Generally, a temperature greater than about 175°F is necessary if  
5 chemical sanitization has not been utilized in the cleaning stage. In a preferred embodiment, chemical sanitization is used in the cleaning stage, and low temperature (140°F to 160°F) rinsing is performed.

In a typical embodiment of the invention, the water  
10 pressure during the rinsing stage is at least about 20 lb/in<sup>2</sup>. Additionally, the flow rate is at least 5 to 6 gal/min. This combination of flow rate and pressure ensures proper ware contact with the rinse agent.

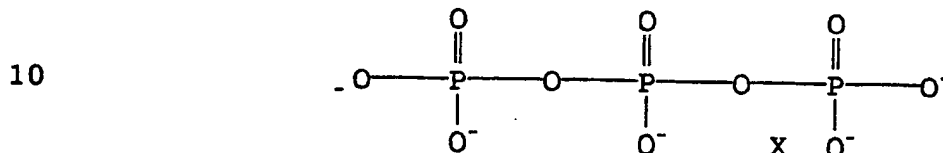
Various modifications and alterations of this  
15 invention will become apparent to those skilled in the art without departing from the scope and spirit of this invention.

## WE CLAIM:

1. An improved method of warewashing comprising:
  - (a) contacting ware with a cleaning solution in a cleaning stage, and then
  - 5 (b) contacting the ware with a rinse agent in a rinsing stage, the rinse agent comprising an aqueous solution of an effective deposit modifying amount of a deposit modifier comprising a compound that causes the formation of a clear coating of
  - 10 deposits.
2. The improved method of warewashing of claim 1 wherein the concentration of the deposit modifier in the rinse agent is about 300 to 20,000 ppm by weight of the
- 15 rinse agent.
3. The improved method of warewashing of claim 1 wherein the deposit modifier comprises at least 3 hydrogen bonding groups selected from the group
- 20 consisting of a carboxy, phospho, a phosphono, amino, hydroxy, sulfo, sulfono, derivatives thereof and mixtures thereof.
4. The improved method of claim 3 wherein the
- 25 hydrogen bonding groups comprise three carboxy groups.
5. The improved method of claim 3 wherein the hydrogen bonding groups comprise two carboxy groups and a hydroxy group.
- 30
6. The improved method of claim 3 wherein the hydrogen bonding groups comprise a carboxy, a sulfono and an amino group.
- 35
7. The improved method of claim 3 wherein the deposit modifier comprises two carboxy groups and at least one more hydrogen bonding group selected from the

group consisting of a carboxy, a hydroxy, an amino, a sulfo, a sulfono, a phosphono, a phospho, derivatives thereof and mixtures thereof.

5        8.    The improved method of claim 3 wherein the deposit modifier is selected from the group of deposit modifiers consisting of the general formula:



15 wherein X = 1 to 20.

9. The improved method of warewashing of claim 1 wherein the deposit modifier is selected from the group consisting of the sodium salts of: tripolyphosphate, ethylene diamine tetraacetic acid, nitrilo triacetic acid, citric acid, lactic acid, gluconic acid, 2-phosphonobutane-1,2,4-tricarboxylic acid, 1-hydroxethylidene-1,1-diphosphonic acid, hexametaphosphate, tartaric acid, aspartic-N,N-diacetic acid, beta-alanine-N,N-diacetic acid, malic acid, sulfosuccinic acid, and aspartic acid; polymers or copolymers of acrylic acid, maleic acid and acrylamide methyl propane sulfonate; and the sugars: sorbitol, galactose, maltose, glucose, sucrose and lactose.

10. The improved method of warewashing of claim 1 wherein the deposit modifier causes a clear coating of deposits with an average thickness of about 5 nm to 2  $\mu$ m to remain on the ware after the rinsing stage.

11. The improved method of warewashing of claim 1 wherein the service water has a total dissolved solids level less than about 1,500 ppm.

12. In a method of warewashing wherein ware is contacted with a cleaning solution in a cleaning stage, and then contacted with a rinse agent in a rinsing stage, wherein the improvement comprises the steps of:  
5 contacting the ware in the rinsing stage with an effective deposit modifying amount of a deposit modifier comprising a compound causing the formation of a clear coating of deposits.

10 13. The method of claim 12 wherein the effective deposit modifying amount of the deposit modifier is about 300 to 20,000 ppm of the rinse agent.

15 14. The method of claim 12 wherein the deposit modifier comprises at least three hydrogen bonding groups selected from the group consisting of carboxy, phospho, phosphono, amino, hydroxy, sulfo, sulfono, derivatives thereof and mixtures thereof.

20 15. The method of claim 12 wherein the deposit modifier is selected from the group consisting of the sodium salts of: tripolyphosphate, ethylene diamine tetraacetic acid, nitrilo triacetic acid, citric acid, lactic acid, gluconic acid, 2-phosphonobutane-1,2,4-  
25 tricarboxylic acid, 1-hydroxethylidene-1,1-diphosphonoic acid, hexametaphosphate, tartaric acid, aspartic-N,N-diacetic acid, beta-alanine-N,N-diacetic acid, malic acid, sulfosuccinic acid, and aspartic acid; polymers or copolymers of acrylic acid, maleic acid and acrylamide  
30 methyl propane sulfonate; and the sugars: sorbitol, galactose, maltose, glucose, sucrose and lactose.

16. The method of claim 12 wherein a clear coating of non-volatile deposits with an average thickness  
35 remains of 5 nm to 2 $\mu$ m on the ware after the rinsing stage.

17. The method of claim 12 wherein a service water, utilized in the clean solution and the rinse agent, comprises about 600 to 1500 ppm total dissolved solids.

5 18. The method of claim 16 wherein the clear coating of non-volatile deposits comprises:

- (a) non-volatile components from a service water;
- (b) the deposit modifier; and
- 10 (c) water.

19. A rinse agent comprising a concentrated source of a deposit modifier comprising a compound that causes the formation of a clear coating of deposits.

15

20. The rinse agent of claim 19 wherein the concentrated source of the deposit modifier comprising a compound that causes the formation of a clear coating of deposits comprises a concentrated liquid with about 10  
20 to 60% by weight active deposit modifier.

21. The rinse agent of claim 19 wherein the concentrated source of the deposit modifier comprises a concentrated solid with about 60 to 90% by weight of the  
25 active deposit modifier.

22. The rinse agent of claim 19 wherein the rinse agent comprises less than 1 part by weight of a surfactant for every 10 parts of all other components in  
30 the rinse agent excluding water.

23. A rinse agent comprising an aqueous solution comprising an effective deposit modifying amount of a mixture of two or more deposit modifiers comprising a  
35 compound causing a clear coating of deposits to form wherein the deposit modifiers comprise at least 3 hydrogen bonding groups selected from the groups

consisting of carboxy, phospho, phosphono, amino, hydroxy, sulfo, sulfono, derivatives thereof and mixtures thereof.

5        24. The rinse agent of claim 23 wherein the rinse agent comprises about 300 to 20,000 ppm of the mixture of two or more deposit modifiers.

10        25. The rinse agent of claim 23 wherein the deposit modifiers are selected from the group consisting of the sodium salts of: tripolyphosphate, ethylene diamine tetraacetic acid, nitrilo triacetic acid, citric acid, lactic acid, gluconic acid, 2-phosphonobutane-1,2,4-tricarboxylic acid, 1-hydroxethylidene-1,1-diphosphonoic  
15        acid, hexametaphosphate, tartaric acid, aspartic-N,N-diacetic acid, beta-alanine-N,N-diacetic acid, malic acid, sulfosuccinic acid, and aspartic acid; polymers or copolymers of acrylic acid, maleic acid and acrylamide methyl propane sulfonate; and the sugars: sorbitol,  
20        galactose, maltose, glucose, sucrose and lactose.

26. The rinse agent of claim 23 wherein the mixture of two or more deposit modifiers comprises at least one pair of deposit modifiers selected from the group  
25        consisting of sodium tripolyphosphate and hexametaphosphate, sodium citrate and sodium gluconate, ethylene tetraacetic acid and nitrilotriacetic acid, aspartic-N,N-diacetic acid and beta-alanine-N,N-diacetic acid and salts thereof.

30

27. The rinse agent of claim 23 wherein there is less than 1 part by weight of a surfactant for every 10 parts of all other components in the rinse agent excluding water.

35

28. A ware article comprising a clear coating of deposits on the piece of ware.

29. The ware article according to claim 28 wherein the clear coating of deposits comprises:

- 5 (a) non-volatile components from a service water;
- (b) a deposit modifier; and
- (c) water.

30. The ware article according to claim 28 wherein  
10 the clear coating of deposits has an average thickness of about 5.0 nm to 2.0  $\mu$ m.

31. The ware article according to claim 28 wherein the clear coating of mineral deposits is formed by  
15 contacting the ware with a cleaning solution in a cleaning stage and then contacting the ware with an aqueous solution of an effective deposit modifying amount of a deposit modifier comprising a compound that causes the formation of a clear coating of deposits on  
20 the ware in a rinsing stage.

32. The ware article according to claim 31 wherein the deposit modifier comprises at least three hydrogen bonding groups selected from the group consisting of  
25 carboxy, phospho, phosphono, amino, hydroxy, sulfo, sulfono, derivatives thereof and mixtures thereof.

33. A clear coating of non-volatile deposits comprising:

- 30 (a) non-volatile components from a service water;
- (b) a deposit modifier; and
- (c) water.

35 34. The clear coating of claim 33 resulting from contacting ware with a rinse agent comprising an aqueous solution of an effective deposit modifying amount of a



deposit modifier comprising a compound that causes the formation of a clear coating of deposits.

## INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 94/02208

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 C11D3/37 C11D7/16 C11D7/26 C11D7/32 C11D7/34  
C11D7/36

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C11D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

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A	FR,A,1 259 820 (BELAIEFF R.) 11 August 1961 see the whole document ---	1-34
A	FR,A,1 069 342 (CHEMISCHE FABRIK BUDENHEIM A. G.) 6 July 1954 see page 2, left column, line 43 - line 47; claims ---	1-34
A	DE,C,41 24 372 (DOMEX AQUA TEC GMBH) 29 October 1992 see the whole document ---	1-34
-/--		

☒ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

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Date of the actual completion of the international search

17 February 1995

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# INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 94/02208

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